

### Three New Sesquiterpenes from *Laggera pterodonta*

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A new eremophilane sesquiterpene, (2 $\beta$ )-2-deoxo-2-methoxytessaric acid (**1**), and two new eudesmane sesquiterpenes, (3 $\beta$ ,10 $\alpha$ )-3-methoxyeudesma-4,11(13)-dien-12-oic acid (**2**) and (3 $\alpha$ ,4 $\beta$ ,8 $\alpha$ )-4-(acetyloxy)-3-(2,3-dihydroxy)-2-methyl-1-oxobutoxy-8-hydroxyeudesm-7(11)-eno-12,8-lactone (**3**), along with the ten known compounds **4–13** were isolated from the aerial parts of *Laggera pterodonta*. The structures of the new compounds were elucidated by spectroscopic analyses, including 2D-NMR data.

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**Introduction.** – *Laggera pterodonta* (DC.) BENTH. (Compositae), widely distributed in the southwest of China, especially in Yunnan Province, has been used as folk medicine since ancient times. Pharmacological investigations have indicated that the extract of *L. pterodonta* has antileukaemia, antibacterial, anti-inflammatory, and antimalarial activities [1]. Previous research has also revealed that flavonols, which account for the anti-inflammatory activity [2], and eudesmane sesquiterpenes represent the main secondary metabolites of this plant [3][4]. Until now, more than 60 sesquiterpenoids were isolated from *L. pterodonta* [5]. In the course of our systematic search for bioactive compounds from Chinese medicinal herbs, the aerial parts of *L. pterodonta* were studied, and a new eremophilane sesquiterpene, (2 $\beta$ )-2-deoxo-2-methoxytessaric acid<sup>1)</sup> (**1**), and two new eudesmane sesquiterpenes, (3 $\beta$ ,10 $\beta$ )-3-methoxyeudesma-4,11(13)-dien-12-oic acid<sup>1)</sup> (**2**) and (3 $\alpha$ ,4 $\beta$ ,8 $\alpha$ )-4-(acetyloxy)-3-(2,3-dihydroxy)-2-methyl-1-oxobutoxy)-8-hydroxyeudesm-7(11)-eno-12,8-lactone<sup>1)</sup> (**3**), along with the ten known compounds **4–13** were isolated (eremophilane = (1*S*,4*aR*,7*R*,8*aR*)-decahydro-1,8*a*-dimethyl-7-(1-methylethyl)naphthalene; eudesmane = (1*R*,4*aR*,7*R*,8*aS*)-decahydro-1,4*a*-dimethyl-7-(1-methylethyl)naphthalene). Compounds **1–13** were tested for anti-inflammatory and cytotoxic activity, but none of them showed any activity. Herein, we report the isolation and structural elucidation of these secondary metabolites.

**Results and Discussion.** – Purification of the AcOEt extract led to the isolation of the three new compounds **1–3**, together with the ten known analogues 14,5 $\alpha$ -

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<sup>1)</sup> Trivial atom numbering; for systematic names, see *Exper. Part*.

epoxyeudesm-11(13)-en-12-oic acid (**4**) [6], 5 $\beta$ -hydroxycostic acid (**5**) [6], 5 $\alpha$ -hydroxycostic acid (**6**) [6], 5 $\alpha$ -hydroxy-4 $\alpha$ ,14-dihydrocostic acid (**7**) [6], 4 $\alpha$ ,5 $\alpha$ -dihydroxyeudesm-11(13)-en-12-oic acid (**8**) [1], ilicic acid (**9**) [7], 4-*O*-acetyl-3-*O*-(2,3-epoxy-2-methylbutanoyl)cuauthemone (**10**) [8], 4-*O*-acetyl-3-*O*-[3-(acetyloxy)-2-methyl-2-hydroxybutanoyl]cuauthemone (**11**) [9], 3-*O*-(2,3-epoxy-2-methylbutanoyl)cuauthemone (**12**) [8], and 3-*O*-(2,3-dihydroxy-2-methylbutyryl)cuauthemone (**13**) [10] (Fig. 1).

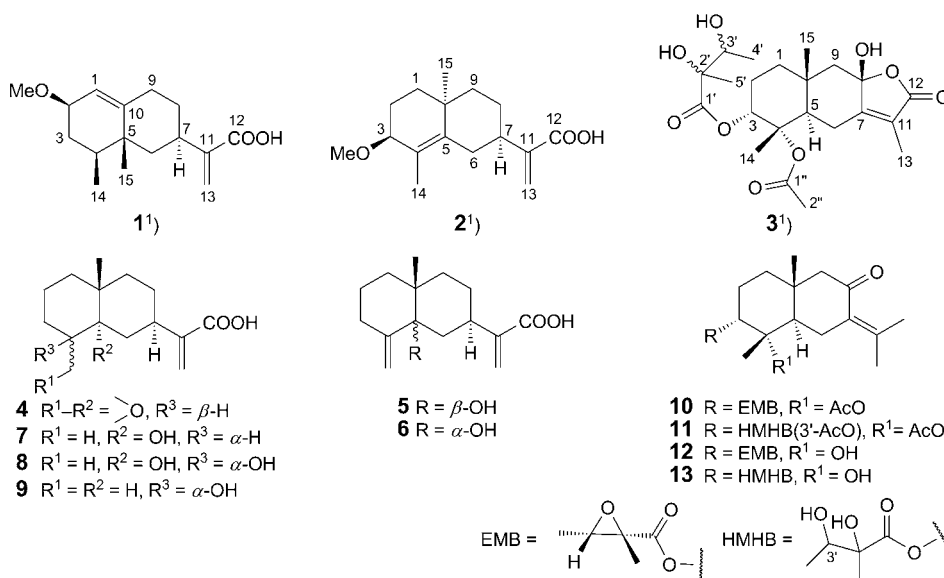
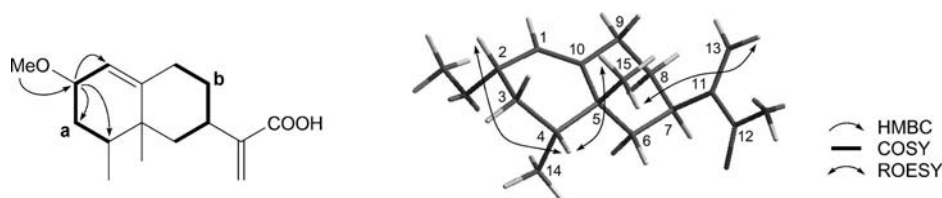


Fig. 1. Compounds **1–13**, isolated from *Laggera pterodonta*

Compound **1**, an optically active, colorless oil, had the molecular formula  $\text{C}_{16}\text{H}_{24}\text{O}_3$  as established by HR-ESI-MS ( $[M + \text{Na}]^+$  at  $m/z$  287.1627). The IR absorption bands at 3432 and 1692  $\text{cm}^{-1}$  implied the presence of a conjugated carboxylic acid group. In addition to a MeO group ( $\delta(\text{H})$  3.43;  $\delta(\text{C})$  56.1), 15 C-atoms were observed in the  $^{13}\text{C}$ -NMR spectrum (Table 1), arising from two Me groups ( $\delta(\text{C})$  15.5 and 19.1), five  $\text{CH}_2$  groups ( $\delta(\text{C})$  28.1, 29.5, 31.9, 40.3, and 124.5), four CH groups ( $\delta(\text{C})$  31.7, 32.8, 73.2, and 120.4), and four quaternary C-atoms ( $\delta(\text{C})$  38.6, 144.9, 149.3, and 172.1). Correlations in the  $^1\text{H}$ ,  $^1\text{H}$ -COSY and HSQC plots revealed the presence of two proton-bearing structural fragments,  $\text{CHCHCH}_2\text{CHMe}$  (**a**) and  $\text{CH}_2\text{CHCH}_2\text{CH}_2$  (**b**; Fig. 2). Detailed HMBC analysis suggested that the structure of **1** was very similar to that of tessaric acid (= (2*R*,8*S*,8*aR*)-1,2,3,4,6,7,8,8*a*-octahydro-8,8*a*-dimethyl- $\alpha$ -methylene-6-oxonaphthalene-2-acetic acid), a known eremophilane derivative [11]. The main difference between the two compounds was that the C=O group in tessaric acid was replaced by an oxygenated methine group in **1** as deduced from the HMBC cross-peaks of  $\delta(\text{H})$  5.56 ( $d$ ,  $J = 3.7$  Hz, H–C(1)), 1.69 ( $H_\beta$ –C(3)), and 1.83 (H–C(4)) (see Table 2) with  $\delta(\text{C})$  73.2 ( $d$ , C(2)) (Fig. 2). In addition, the MeO signal at  $\delta(\text{H})$  3.43 correlated with C(2), suggesting that the MeO group is located at C(2). The relative configuration of **1** was determined by a

Table 1.  $^{13}\text{C}$ -NMR Data (100 MHz,  $\text{CDCl}_3$ ,  $27^\circ$ ) of **1–3**).  $\delta$  in ppm.

C-Atom	<b>1</b>	<b>2</b>	<b>3</b>
C(1)	120.4 ( <i>d</i> )	34.2 ( <i>t</i> )	33.7 ( <i>t</i> )
C(2)	73.2 ( <i>d</i> )	21.9 ( <i>t</i> )	23.6 ( <i>t</i> )
C(3)	31.9 ( <i>t</i> )	79.2 ( <i>d</i> )	78.2 ( <i>d</i> )
C(4)	31.7 ( <i>d</i> )	124.7 ( <i>s</i> )	71.9 ( <i>s</i> )
C(5)	38.6 ( <i>s</i> )	140.1 ( <i>s</i> )	51.1 ( <i>d</i> )
C(6)	28.1 ( <i>t</i> )	31.2 ( <i>t</i> )	21.1 ( <i>t</i> )
C(7)	32.8 ( <i>d</i> )	39.9 ( <i>d</i> )	161.1 ( <i>s</i> )
C(8)	29.5 ( <i>t</i> )	27.9 ( <i>t</i> )	103.3 ( <i>s</i> )
C(9)	40.3 ( <i>t</i> )	41.9 ( <i>t</i> )	53.7 ( <i>t</i> )
C(10)	149.3 ( <i>s</i> )	34.2 ( <i>s</i> )	34.9 ( <i>s</i> )
C(11)	144.9 ( <i>s</i> )	145.3 ( <i>s</i> )	121.9 ( <i>s</i> )
C(12)	172.1 ( <i>s</i> )	170.4 ( <i>s</i> )	172.3 ( <i>s</i> )
C(13)	124.5 ( <i>t</i> )	123.9 ( <i>t</i> )	8.1 ( <i>q</i> )
C(15)	15.5 ( <i>q</i> )	22.9 ( <i>q</i> )	21.0 ( <i>q</i> )
C(14)	19.1 ( <i>q</i> )	17.3 ( <i>q</i> )	18.7 ( <i>q</i> )
MeO or C(1')	56.1 ( <i>q</i> )	56.8 ( <i>q</i> )	170.1 ( <i>s</i> )
C(2')			76.3 ( <i>s</i> )
C(3')			74.5 ( <i>d</i> )
C(4')			13.2 ( <i>q</i> )
C(5')			21.5 ( <i>q</i> )
MeCO			174.7 ( <i>s</i> ), 22.0 ( <i>q</i> )

Fig. 2. Key 2D correlations of **1**<sup>1</sup>

ROESY analysis (Fig. 2); the correlations  $\text{H-C}(2)/\text{H-C}(4)$ ,  $\text{H}_b\text{-C}(13)/\text{Me}(14)$ ,  $\text{H}_b\text{-C}(13)/\text{Me}(15)$ , and  $\text{H}_a\text{-C}(13)/\text{H-C}(7)$  indicated the  $\alpha$ -orientation of  $\text{H-C}(2)$  and  $\text{H-C}(4)$ , and  $\beta$ -orientation of  $\text{Me}(14)$  and  $\text{Me}(15)$ . Since **1** had a specific rotation ( $[\alpha]_{20}^D = -166.2$ ) similar to that of tessaric acid, ( $[\alpha] = -156.2$ ) whose absolute configuration was established by X-ray single-crystal diffraction [12], the absolute configuration of **1** should be the same as that of tessaric acid. Thus, the structure of **1** was deduced as (2 $\beta$ )-2-deoxo-2-methoxytessaric acid<sup>1</sup>.

The HR-ESI-MS of **2** gave a  $[M + \text{Na}]^+$  peak at  $m/z$  287.1618, corresponding to the molecular formula  $\text{C}_{16}\text{H}_{24}\text{O}_3$ . The IR absorption at  $1706\text{ cm}^{-1}$  indicated the presence of a  $\text{C=O}$  group. The  $^1\text{H}$ -NMR spectrum (Table 2) revealed the presence of two olefinic H-atoms ( $\delta(\text{H})$  5.58 and 6.28 (2 br. s)), one MeO group ( $\delta(\text{H})$  3.35 (*s*)), and two Me groups ( $\delta(\text{H})$  1.02 and 1.72 (2 *s*)). The  $^{13}\text{C}$ -NMR data of **2** (Table 1) showed close resemblance to those of eudesma-4,11(13)-dien-12-oic acid [13], but with an additional MeO group ( $\delta(\text{H})$  3.35 and  $\delta(\text{C})$  56.8). The MeO group was connected to C(3) as

Table 2.  $^1\text{H-NMR}$  Data (400 MHz,  $\text{CDCl}_3$ ,  $27^\circ$ ) of **1–3**<sup>1</sup>.  $\delta$  in ppm,  $J$  in Hz.

H-Atom	<b>1</b>	<b>2</b>	<b>3</b>
H–C(1)	5.56 ( <i>d</i> , $J=3.7$ )	1.26–1.58, 1.60–1.68 ( <i>2m</i> )	1.25–1.39 ( <i>m</i> )
H–C(2) or $\text{CH}_2(2)$	3.57 ( <i>br. s</i> )	1.60–1.68, 1.89–1.92 ( <i>2m</i> )	1.88–1.96, 1.70–1.75 ( <i>2m</i> )
$\text{CH}_2(3)$ or H–C(3)	1.52 ( <i>ddd</i> , $J=18.8, 17.9, 7.0$ ), 1.69–1.76 ( <i>m</i> )	3.41 ( <i>s</i> )	4.90 ( <i>t</i> , $J=2.2$ )
H–(4)	1.78–1.90 ( <i>m</i> )	–	–
$\text{CH}_2(6)$	1.66–1.75 ( <i>m</i> )	1.72–1.79 ( <i>m</i> ), 2.65 ( <i>d</i> , $J=13.2$ )	2.16–2.50 ( <i>m</i> ), 2.97 ( <i>dd</i> , $J=13.3, 2.5$ )
H–C(7)	2.61–2.63 ( <i>m</i> )	2.45 ( <i>t</i> , $J=11.6$ )	–
$\text{CH}_2(8)$	1.78–1.90 ( <i>m</i> ), 1.68 ( <i>dd</i> , $J=23.3, 9.7$ )	1.26–1.58, 1.72–1.79 ( <i>2m</i> )	–
$\text{CH}_2(9)$	2.45 ( <i>dd</i> , $J=22.2, 9.6$ ), 2.07 ( <i>dd</i> , $J=13.5, 7.8$ )	1.26–1.58, 1.60–1.68 ( <i>2m</i> )	1.52, 2.19 ( <i>2d</i> , each $J=13.4$ )
$\text{CH}_2(13)$ or Me(13)	5.64, 6.26 ( <i>2s</i> )	5.58, 6.28 ( <i>2br. s</i> )	1.99 ( <i>s</i> )
Me(14)	0.84 ( <i>s</i> )	1.72 ( <i>s</i> )	1.20 ( <i>s</i> )
Me(15)	0.86 ( <i>s</i> )	1.02 ( <i>s</i> )	1.11 ( <i>s</i> )
MeO	3.43 ( <i>s</i> )	3.35 ( <i>s</i> )	–
H–C(3')	–	–	5.16 ( <i>q</i> , $J=6.3$ )
Me(4')	–	–	1.30 ( <i>d</i> , $J=5.6$ )
Me(5')	–	–	1.28 ( <i>s</i> )
MeCO	–	–	1.80 ( <i>s</i> )

deduced from HMBCs of  $\delta(\text{H})$  1.72 (*s*, Me(14)), 1.32 (*m*,  $\text{H}_\alpha\text{-C}(1)$ ), 1.57 (*m*,  $\text{H}_\beta\text{-C}(1)$ ), and 3.35 (*s*, MeO) with 79.2  $\delta(\text{C})$  (*d*, C(3)). In the ROESY plot, the correlations H–C(3)/Me(15) and H–C(7)/Me(15) were observed, which indicated  $\alpha$ -orientation of H–C(3), H–C(7), and Me(15). Therefore, the structure of compound **2** was deduced as (3 $\beta$ ,10 $\alpha$ )-3-methoxyeudesma-4,11(13)-dien-12-oic acid.

Compound **3** had a molecular formula  $\text{C}_{22}\text{H}_{32}\text{O}_9$  as inferred from the HR-ESI-MS ( $m/z$  463.1951 [ $M + \text{Na}$ ]<sup>+</sup>). Its IR spectrum showed an  $\alpha,\beta$ -unsaturated  $\gamma$ -lactone absorption ( $1739\text{ cm}^{-1}$ ). Except for the presence of a-2,3-dihydroxy-2-methylbutanoyl group ( $\delta(\text{H})$  1.30 (*d*,  $J=5.6\text{ Hz}$ , Me(4')), 1.28 (*s*, Me(5')); and 5.16 (*q*,  $J=6.3\text{ Hz}$ , H–C(3)); C(1') to C(5') at  $\delta(\text{C})$  170.1 (*s*), 76.3 (*s*), 74.5 (*d*), 13.2 (*q*), and 21.5 (*g*)) and an AcO group ( $\delta(\text{C})$  22.0 (*q*) and 174.7 (*s*);  $\delta(\text{H})$  1.80 (*s*) as deduced from HSQC and HMBC spectra, compound **3** possessed 15 other C-atoms signals. Detailed analysis of 2D-NMR data (Fig. 3) suggested that **3** should be an eudesmane sesquiterpene endowed with an  $\alpha,\beta$ -unsaturated  $\gamma$ -lactone moiety ( $\delta(\text{C})$  121.9, 161.1, and 172.3 (3 *s*)), as in the closely related (3 $\alpha$ ,4 $\beta$ ,8 $\alpha$ , -3,4,8-trihydroxyeudesm-7(11)-eno-12,8-lactone [14]. According to the HMBC cross-peak  $\delta(\text{H})$  4.90 (*t*,  $J=2.2\text{ Hz}$ , H–C(3))/ $\delta(\text{C})$  170.1 (C(1')), the (2,3-dihydroxy-2-methylbutanoyl)oxy group should be located at C(3). In the ROESY plot, the correlations H–C(5)/MeC=O were observed. This suggested that the Ac group was bound to O–C(4). The relative configuration was established by the ROESY experiment, the correlations Me(14)/Me(15) and H–C(3)/Me(15) being observed. Thus, the (2,3-dihydroxy-2-methylbutanoyl)oxy and AcO groups are  $\alpha$ -oriented. The configuration of OH–C(8) was thought to be  $\beta$ , because the chemical shift of Me(15) was influenced by a deshielding effect of OH–C(8), similar to

that of 8 $\beta$ -hydroxyxitlixochilin 4-*O*-acetate [8]. Therefore, the structure of **3** was determined as (3 $\alpha$ ,4 $\beta$ ,8 $\alpha$ )-4-(acetyloxy)-3-(2,3-dihydroxy-2-methyl-1-oxobutoxy)-8-hydroxyeudesm-7(11)-eno-12,8-lactone.

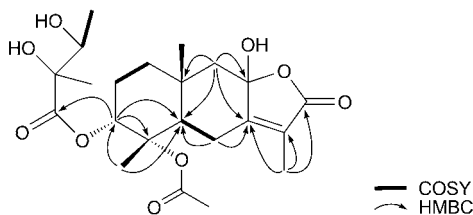


Fig. 3. Key 2D correlations of **3**

The presence of compounds **1–7** and **10–13** in *L. pterodonta* is reported for the first time. All compounds were tested for anti-inflammatory and cytotoxic activity *in vitro*. However, none of them exhibited such an activity.

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### Experimental Part

**General.** Column chromatography (CC): silica gel (SiO<sub>2</sub>, 200–300 mesh; Qingdao Haiyang Chemical Co. Ltd.), RP-18 gel (20–45  $\mu$ m, Fuji Silysia Chemical Ltd.), and Sephadex LH-20 (Pharmacia Fine Chemical Co., Ltd.). TLC: SiO<sub>2</sub> GF 254 (Qingdao Haiyang Chemical Co., Ltd.); detection by spraying with 10% H<sub>2</sub>SO<sub>4</sub> in EtOH followed by heating. Optical rotations: Horiba-SEPA-300 polarimeter. UV Spectra: Shimadzu-UV-2401A spectrophotometer;  $\lambda_{\max}$  (log  $\epsilon$ ) in nm. IR Spectra: Tenor-27 spectrophotometer; KBr pellets;  $\tilde{\nu}$  in cm<sup>-1</sup>. 1D- and 2D-NMR Spectra: Bruker-DRX-500 and -AM-400 spectrometers;  $\delta$  in ppm rel. to Me<sub>4</sub>Si as internal standard, *J* in Hz. EI-MS: VG-Autospec-3000 spectrometer; in *m/z*. HR-ESI-MS: API-QSTAR-Pulsar-1 spectrometer; in *m/z*.

**Plant Material.** The aerial parts of *L. pterodonta* were bought on the market of Chinese traditional medicine in Kunming, Yunnan Province, P. R. China, in April 2011, and identified by Prof. Xiao Cheng, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen (No. 20110704) has been deposited with the Kunming Institute of Botany, Chinese Academy of Sciences.

**Extraction and Isolation.** The aerial parts of *L. pterodonta* (9 kg) were extracted exhaustively with 95% EtOH at r.t. The EtOH extract was concentrated, and the residue extracted with AcOEt to yield a residue (400 g). This residue was subjected to CC (SiO<sub>2</sub> (2.5 kg, 150  $\times$  12 cm), petroleum ether/acetone 20:1  $\rightarrow$  1:1): Fractions 1–5. Fr. 3 (80 g) was subjected to medium-pressure liquid chromatography (MPLC) (MCI (1 kg), H<sub>2</sub>O, 60, 70, 80, 90, and 100% MeOH (4 l for each gradient): Fr. 3a–Fr. 3e. After repeated CC (SiO<sub>2</sub> (100 g, 60  $\times$  4 cm), CHCl<sub>3</sub>/acetone 100:1  $\rightarrow$  1:1), Fr. 3a (4.8 g) afforded **12** (37 mg). Fr. 3b (17.4 g) was further applied to CC (SiO<sub>2</sub> (400 g, 120  $\times$  4 cm), CHCl<sub>3</sub>/AcOEt 100:1  $\rightarrow$  1:1): **4** (81 mg), **5** (100 mg), **6** (580 mg), **7** (80 mg), **10** (2.6 g), and **11** (460 mg). Fr. 4 (85 g) was separated by MPLC (MCI (1 kg), H<sub>2</sub>O, 50, 60, 70, 80, 90, and 100% MeOH (4 l for each gradient)): Fr. 4a–Fr. 4d. Fr. 4a (9.4 g) was further applied to CC (SiO<sub>2</sub> (200 g, 70  $\times$  4 cm), CHCl<sub>3</sub>/MeOH 100:1  $\rightarrow$  1:1): **8** (30 mg) and **9** (6.8 g). Fr. 4b (18.6 g) was subjected to CC (SiO<sub>2</sub> (400 g, 120  $\times$  4 cm), petroleum ether/PrOH 100:1  $\rightarrow$  1:1): **3** (5 mg), **13** (45 mg), and Fr. 4b1 (90 mg). Fr. 4b1 was further purified by prep. HPLC (RP-18, 58% MeOH/H<sub>2</sub>O): **1** (8 mg) and **2** (6 mg).

(2 $\beta$ )-2-Deoxo-2-methoxytessaric Acid (= (2R,6R,8S,8aR)-1,2,3,4,6,7,8,8a-Octahydro-6-methoxy-8,8a-dimethyl- $\alpha$ -methylenenaphthalene-2-acetic Acid; **1**): Colorless oil (CHCl<sub>3</sub>).  $[\alpha]_D^{20} = -166.2$  (c 0.25,

$\text{CHCl}_3$ ). UV ( $\text{CHCl}_3$ ): 239 (2.93), 222 (2.52). IR (KBr): 3432, 2933, 1692, 1625, 1461, 1190, 1080, 932. HR-ESI-MS (pos.): 287.1627 ( $[M + \text{Na}]^+$ ; calc. 287.1623).

(3 $\beta$ ,10 $\beta$ )-3-Methoxyeudesma-4,11(13)-dien-12-oic Acid (=rel-(2R,4aR,7S)-1,2,3,4,4a,6,7-Octahydro-7-methoxy-4a,8-dimethyl- $\alpha$ -methylenenaphthalene-2-acetic Acid; **2**): Colorless oil ( $\text{CHCl}_3$ ).  $[\alpha]_D^{20} = +54.5$  ( $c = 0.20$ ,  $\text{CHCl}_3$ ). UV ( $\text{CHCl}_3$ ): 239 (3.30), 221 (2.87). IR (KBr): 3465, 2939, 1706, 1150, 1067, 864, 494, 442. HR-ESI-MS (pos.): 287.1618 ( $[M + \text{Na}]^+$ , calc. 287.1623).

(3a,4b,8a)-4-(Acetyloxy)-3-(2,3-dihydroxy)-2-methyl-1-oxobutoxy)-8-hydroxyeudesm-7(11)-eno-12,8-lactone (=rel-(4aR,5S,6R,8aR,9aS)-5-(Acetyloxy)-9a-hydroxy-3,5,8a-trimethyl-2-oxo-2,4,4a,5,6,7,8,8a,9,9a-decahydronaphtho[2,3-b]furan-6-yl 2,3-Dihydroxy-2-methylbutanoate; **3**). White, amorphous powder ( $\text{CHCl}_3$ ).  $[\alpha]_D^{20} = -19.9$  ( $c = 0.19$ ,  $\text{CHCl}_3$ ). UV ( $\text{CHCl}_3$ ): 366 (1.41), 238 (2.97), 221 (2.54). IR (KBr): 3437, 2927, 1739, 1376, 1252. HR-ESI-MS (pos.): 463.1951 ( $[M + \text{Na}]^+$ ; calc. 463.1944).

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